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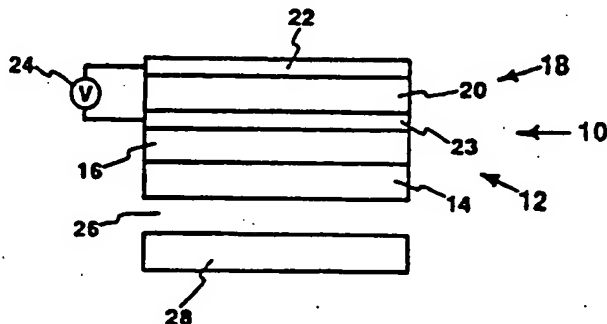
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(54) Title: OPTICAL SENSOR WITH ELECTROLUMINESCENT LIGHT SOURCE AND POLYMER LIGHT DETECTOR



(57) Abstract

An optical sensor (10) is produced with a polymer based light source (18) and/or polymer based light detector (28). An electroluminescent source (18) has a conducting polymer layer (20) or alternatively a phosphor layer (23). A detector (28), of either Schottky or heterojunction/hybrid type, has a photoconductive polymer layer (64) or adjacent conducting polymer (76) and semiconductor (78) layers where at least one is photoconducting.

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**OPTICAL SENSOR WITH ELECTROLUMINESCENT LIGHT SOURCE
AND POLYMER LIGHT DETECTOR**

Background of the Invention

The invention relates generally to optical sensors
5 and more particularly to light source-transducer-detector
structures and materials for optical sensors.

A variety of fiber optic based and other chemical
sensors have been developed, based on absorbance,
fluorescence, refractive index and other effects. These
10 sensor designs can incorporate a wide range of sensor
chemistries and are thus capable of detecting virtually any
desired target species. These sensors have diverse
applications from environmental monitoring to medical
diagnostics.

15 A common problem to all optical sensors is the
constraints imposed by available light sources and detectors.
Typical conventional light sources include LED's, lasers and
lamps. Detectors include photodiodes. Available light
sources and detectors are often limited as to wavelength and
20 power, as well as cost and size. Conventional sensors require
coupling schemes to effectively input the light from the
source to the transducer portion of the sensor and to return
a light signal from the transducer to the detector. In one
typical arrangement, as illustrated by U.S. Patent 5,059,790,
25 the source and detector are positioned at the distal end of
an optical fiber from the transducer (reservoir cell). In an
alternate arrangement, as illustrated by U.S. Patent
5,116,759, the source and detector have been incorporated into
the cell in direct proximity to the transducer.

30 A recent development is an electroluminescent device
made from a light emitting doped polymer, as described in
Grem, et al., "Realization of a Blue-Light-Emitting Device
Using Poly(p-phenylene)," Adv. Mater. 4(1), Jan. 1992, pp 36-
37; Cao et al., "Solution-cast films of polyaniline: Optical-
35 quality transparent electrodes," Appl. Phys. Lett. 60(22), 1
June 1992, pp 2711-2713; and Gustafsson, et al., "Flexible
light-emitting diodes made from soluble conducting polymers,"
Nature, V. 357, 11 June 1992, pp 477-479. These "polymer

LED's" operate by applying a voltage to a conducting polymer. These polymers are being developed for use in displays in electronic devices. The use of conductive polymers for FETs as well as LEDs is described in Semiconductor International, 5 Jan. 1993, p. 26.

Summary of Invention

According to one aspect of the invention, there is provided an optical sensor, comprising: an optical transducer; an electroluminescent light source operatively coupled to the 10 transducer; a detector operatively coupled to the transducer.

According to another aspect of the invention, there is provided a polymeric light detector, comprising: a conducting polymer layer; a pair of electrodes surrounding the polymer layer, at least one of which electrodes is 15 transparent; means connected to the electrodes for applying a voltage and for detecting an electric current produced in the polymer layer by incident light.

According to a further aspect of the invention, there is preferably an optical sensor comprising an optical 20 transducer, a light source for inputting light into the transducer, and a detector for detecting light from the transducer, wherein at least one of (a) the light source is an electroluminescent light source comprising a layer of electroluminescent polymer and means for applying a voltage 25 to the layer to produce light therefrom, and (b) the detector is a layer of photoconducting polymer and means for detecting a current produced therefrom by incident light.

The invention provides an improved optical sensor, an optical sensor with improved light source and/or detector 30 design and a sandwich type optical sensor having a light source and detector formed therein.

The invention is preferably an optical sensor which has a light emitting polymer as a light source and/or a polymer detector in combination with an optical transducer. 35 The optical transducer can be of any type. The transducer may be essentially a waveguide with or without analyte sensing coating/materials either embedded in or attached on the surface. The transducer could also be a reservoir or other

type cell. A polymer light source is formed on the optical transducer so that light from the source is directly input into the transducer. A suitable detector may also be provided. The detector may be a polymer device which is the reverse of the polymer light source. Alternatively, the light source is conventional and the detector is made of either a conductive polymer or polymer/inorganic semiconductor hybrid. Use of both a polymer source and polymer detector results in a sandwich type design in which the transducer, e.g., a layer of sensing chemistry on a waveguide, is sandwiched between the source and detector polymer layers.

Brief Description of the Drawings

In the accompanying drawings:

Fig. 1 is a cross-sectional view of a simple sensor configuration according to the invention.

Figs. 2A,B illustrate two embodiments of a sandwich sensor according to the invention.

Figs. 3A-C illustrate three embodiments of the invention with an optical fiber.

Fig. 4 is a perspective view of a planar waveguide sensor in accordance with the invention.

Figs. 5A-C illustrate channel waveguide sensors according to the invention.

Fig. 6 is a cross-sectional view of a porous membrane embodiment of the invention.

Fig. 7A-D are cross-sectional views of polymer detector structures.

Detailed Description of the Preferred Embodiments

As shown in Fig. 1, a simplified optical sensor 10 includes an optical transducer 12 which comprises sensing chemistry 14 on substrate 16. Adjacent to the transducer 12 is electroluminescent light source 18 which is formed of light emitting chemistry 20 surrounded by electrodes 22, 23. Voltage source 24 is connected across electrodes 22, 23. Electrode 23 which is between substrate 16 and light emitting chemistry 20 must be transparent. A flow channel 26 is formed in sensor 10 along the exposed face of sensing chemistry 14.

A detector 28 faces sensing chemistry 14 separated by channel 26. Light from source 18 passes directly into transducer 12, through substrate 16, which must be transparent, into sensing chemistry 14. A sample is flowed through channel 26 and
5 interacts with sensing chemistry 14. The transducer may be of any type, e.g. absorption or fluorescence or refractive index. The signal generated by transducer 12 passes across channel 26 into detector 28.

The materials useful for the electroluminescent
10 light source include semiconductor polymers or other organic materials with a necessary bandgap to produce the desired light output. A polymer or other organic material is made semiconductive by the use of a dopant such as sulfonic acid, AsF_5 , I_2 , 2,4,7-trinitro-9-fluorenone, carbazole, sodium,
15 potassium, indium or other metal which produces either electron-hole pairs or electrons or holes in the material. Alternatively, in place of a doped organic material, phosphors can similarly be used to form the electroluminescent layer. In both cases, the layer is very thin, a few microns or less.
20 The electroluminescent layer is placed between a pair of electrodes and a voltage in the range of about 5-10 V is applied. The electrodes must generally be transparent and impedance matched to the layer.

As illustrative examples from the papers cited
25 above, poly(p-phenylene) or PPP was used as the electroluminescent layer, 0.5 micron thick, between indium/tin oxide (ITO) and aluminum (Al) electrodes with a 12 V, 60 Hz voltage applied to produce blue light. Also a substituted poly(1,4-phenylene-vinylene) (MEH-PPV) electroluminescent layer
30 with a soluble polyaniline (PANI-CSA) hole-injecting electrode and calcium electron-injecting electrode and an ITO/MEH-PPV/Ca device have been demonstrated.

Polymers listed below for detectors can also be used
as light sources when used alone or with appropriate
35 dopant(s). The concentration of the dopant may vary from 0.05 % to 20 % based on the polymer weight.

The invention provides a compact solid state sandwich structure particularly with a polymer detector or a hybrid detector made from polymers and inorganic

semiconductors. The sensing chemistry is then basically sandwiched between two polymer layers which form the source and detector. Several variations of the structure result. As shown in Fig. 2A, sensing chemistry 30 is painted onto one side of substrate 32, e.g. a mylar film, and the electroluminescent source 34 is formed on the other side of substrate 32. The details of electroluminescent source 34, e.g. electrodes and light emitting layer, are not shown but are similar to that of Fig. 1. A reverse polymer device (detector) 36 is then formed on one side of a second substrate 38 and the sensing chemistry 30 is sandwiched between substrates 32, 38 with a flow channel 35 between sensing chemistry 30 and substrate 38. The position of the substrate 38 and detector 36 can be reversed, as shown in Fig. 2B.

The optical transducer may be of any type. In particular, the invention can be used with chemical sensors. However, the invention applies generally to all optical sensors. The waveguide type sensors use various forms of waveguides, e.g. fiber optic, channel, or planar. Also used are reservoir type sensors. As shown in Fig. 1, sensor 12 can represent a reservoir cell between source 18 and detector 28. No flow channel may be necessary since the sample may flow directly through the reservoir cell.

As shown in Fig. 3A, electroluminescent light source 42 may be formed on the end of an optical fiber 44 which has a side coated sensing chemistry 46. The detector (not shown) would be placed at the distal end of the fiber 44. However, because of the small surface area of a fiber tip, additional elements can be used to increase the size of the light source. As shown in Fig. 3B, a converging element 48 is placed at the end of fiber 44 to provide a wider surface area for source 42. Alternatively a cone 50 or lens which tapers to a point can be attached to the end of fiber 44 and source 42 formed on the lateral side of cone 50 to increase the area of source 42.

A planar waveguide type sensor can also be used, as shown in Fig. 4. Planar waveguide 54 is formed on substrate 60. Planar waveguide 52 has an electroluminescent light source 54 formed on one end face thereof and detector 56 formed on the opposed end face. Sensing chemistry 58 is

formed on the top surface of waveguide 52. The sensing chemistry 58 may be uniform or patterned.

The polymers used in the light source have characteristics which are highly useful in constructing
5 sensors. Polymers can provide a wide range of wavelengths, and are relatively high power. Since the polymers may initially be in liquid or solution form, uniform coating processes are relatively easy to carry out. The polymers are also flexible which allow various geometries and shapes.

10 The invention can be applied to a channel waveguide. As shown in Figs. 5A,B which show perspective and end views, respectively, a channel waveguide 53 is formed on substrate 60. An electroluminescent light source 54 is placed at one end of channel waveguide 53 and a detector 56 is placed at the
15 opposite end. Sensing chemistry 58 is placed on the top surface of channel waveguide 53. As illustrated, the sensing chemistry 58 is configured in discrete islands in a random pattern; however, other patterns including uniform coating can also be used. Multiple channel waveguides 53a,b can be placed
20 on a single substrate 60, as illustrated in Fig. 5C, each with an electroluminescent light source 54a,b and detector 56a,b. The sensing chemistry 58a,b on each channel waveguide may be different, i.e., specific for different species.

The invention can also be implemented using a porous
25 membrane in place of a conventional substrate. As shown in Fig. 6, sensing chemistry 30 is deposited on a membrane 33, and electroluminescent light source 34 is formed on sensing chemistry 30. Thus, the light source 34 is in direct contact with the sensing chemistry 30. A detector 36 is formed on the
30 opposed face of membrane 33 from sensing chemistry 30. If the membrane 33 and detector 36 are sufficiently porous, a sample will pass through detector 36 and membrane 33 to sampling chemistry 30.

The polymeric detectors that are included in the
35 present invention are of both Schottky barrier or heterojunction type. Figures 7A-D show the cross-sections of detector structures involving polymers.

A polymer-based Schottky type light detector 62 is shown in Fig. 7A. Detector 62 is formed of a conducting

polymer layer 64 between a pair of electrodes 66,68. Light to be detected is incident through electrode 66 onto polymer layer 64. Electrode 66 must thus be light transparent and very thin. Therefore, electrode 66 includes a thicker step portion 70 to which an electrical connection 71 is made. Electrode 68 may be thicker since light does not pass therethrough, and an electrical connection 72 is made thereto. A low voltage is applied across polymer layer 64 between electrodes 66,68 through electrical connections 71,72.

The conductive polymer layer conducts charge, either holes or electrons, depending on the particular material and any dopants. If layer 64 is photoconductive at the wavelength of the incident light to be measured, extra hole-electron pairs are produced by the incident light. The voltage across the layer draws the electrons and holes in opposite directions, toward opposed electrodes 66,68, producing a measurable current flow. This measured current is the detector output signal.

If conductive layer 64 is not photoconductive at the wavelength of interest, the polymer layer 64 is formed of sub-layers 64a,b where sublayer 64a is a conducting polymer and sub-layer 64b, which is at the surface on which the light is incident, is a photoconductive polymer. Sublayer 64b thus acts as a photogenerator to produce the extra charge carriers (holes-electrons) and sublayer 64a is the transport layer across which the charge carriers are transported to produce the detector signal. Sublayer 64b will typically be thin, e.g. 5-10% of the total thickness of the composite layer 64.

Typical dimensions of the polymer detector structure are as follows. Polymer layer 64 is between 1-100 μm , and more preferably 1-10 μm . If a composite layer 64a,b is used, the photoconductive sublayer 64b is 5-10% of the thickness. Electrode 66 through which the light passes is very thin, 5-100 nm, except for the step 70 which is 200-400 nm. Electrode 68 is similar to step 70, 200-400 nm. The transparent electrode is typically tin oxide, but other materials including indium or aluminum could also be used.

Fig. 7B illustrates a similar polymer based Schottky type light detector which is double sided, i.e., light is

incident on either electrode, both of which are configured as electrode 66 of Fig. 7A.

A polymer based heterojunction/hybrid type light detector 74 is shown in Fig. 7C. Detector 74 is formed of a p-type conducting polymer layer 76 adjacent to an n-type semiconductor layer 78 between a pair of electrodes 80,82. Layers 74,76 form a p-n junction. Light is incident through electrode 80 into polymer layer 76 which is photoconductive. This can be done, if necessary, by a photoconducting sublayer. Electrical connections 84 are made to electrodes 80,82 to apply a low voltage and measure current flow. Incident light produces current flow across the p-n junction. The p-type conducting polymer layer 76 is typically 0.1-1.0 μm thick and the n-type semiconductor layer 78 is 10-200 μm thick. Electrode 80 is light transparent and 5-100 nm thick (and would also include a thicker step portion as in electrode 66 of Figs. 7A,B), while electrode 82 may be thicker, 10-400 nm. The n-type semiconductor is a conventional material, e.g., Si, In, GaAs.

Another polymer based heterojunction/hybrid type light detector 86 shown in Fig. 7D is similar to Fig. 7C except that the light is incident through electrode 82 to n-type semiconductor layer 78 which is photoconducting. This also produces current flow across the p-n junction. In this configuration, electrode 82 must be transparent so it is about 5-100nm thick, except for a step portion (not shown) as in electrode 66. The n-type semiconductor layer 78 is thinner, 0.1-10 μm , while the p-type conducting polymer layer 76 is thicker, 1-50 μm . Electrode 80 can be thicker, 10-400 nm.

Polymers that can be used as photoconductive/conductive materials in such detectors include the following and various combinations thereof.

Polythiophene and its derivatives
Polyisothionaphthene
Trans-polyacetylene
Polyphenylene
Copolymer of pyrrole and quinone
Polyquinoline(s)

Polyaniline
Sulfonated polyaniline
Polyarylene vinylene
Polyvinylene
5 Polypyrrole and its derivatives
Poly(n-vinyl carbazole)
Polyphenylmethylsilylene/2,4,7-trinitro-9-fluorenone
Polytetrafluoroethylene
Copolymers of vinylidene fluoride and
10 trifluoroethylene
Blends of polyvinylidene fluoride and
polyalkylmethacrylate(s)
Poly(arylene azomethine)
Poly(arylene sulfurdiimide)
15 Poly(2-N-carbazolyethyl methacrylate)
Poly[S-(w-N carbazolyalkyl)L-Cysteine]
Poly(N-carbazolyethyl glycidyl ether)
Poly(N-methyl-3-hydroxymethylcarbazolyl acrylate-co-
acryloyl-3'-hydroxypropyl 3,5 dinitrobenzoate)
20 Poly[N-(2-hydroxyethyl) carbanolyl methacrylate-co-
methacryloyl- β -hydroxyethyl 3,5-
dinitrobenzoate]
Polymers incorporating metal phthalocyanin moiety,
such as copper phthalocyanine

25 The polymers can be both undoped or doped with an
appropriate dopant such as AsF_5 , I_2 , 2,4,7-trinitro-9-
fluorenone, sodium, potassium, and carbazole and its
derivatives.

Polymeric detectors can include layered
30 photoconductors with a photogenerator and transport-layer.

Inorganic polymers acting as photoconductors in the
detector include polymers with $\{P=N\}$ repeating unit (e.g.,
Poly[bis-(2-naphthyloxyphosphazine)]).

Changes and modifications in the specifically
35 described embodiments can be carried out without departing
from the scope of the invention which is intended to be
limited only by the scope of the appended claims.

CLAIMS

1. An optical sensor, comprising:
an optical transducer;
an electroluminescent light source operatively coupled to the transducer;
a detector operatively coupled to the transducer.
2. The sensor of Claim 1 wherein the electroluminescent light source comprises a layer of electroluminescent material and means for applying a voltage to the layer to produce light therefrom.
3. The sensor of Claim 23 wherein the material is a polymer.
4. The sensor of Claim 2 wherein the electroluminescent material is a phosphor.
5. The sensor of Claim 1 wherein the optical transducer is a waveguide with a sensing chemistry coated thereon.
6. The sensor of Claim 5 wherein the waveguide is a fiber optic.
7. The sensor of Claim 1 wherein the optical transducer is a reservoir cell.
8. The sensor of Claim 1 wherein the optical transducer is a substrate with a sensing chemistry coated on a surface thereof and the electroluminescent light source is formed on an opposed surface of the substrate from the sensing chemistry.

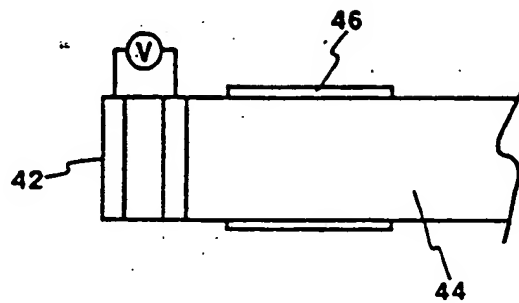
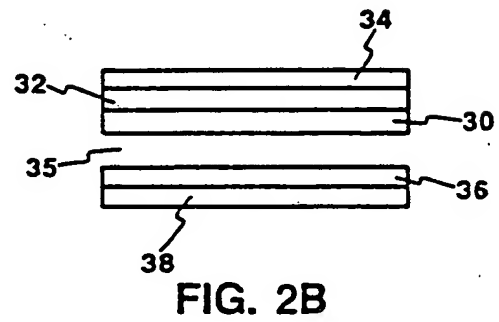
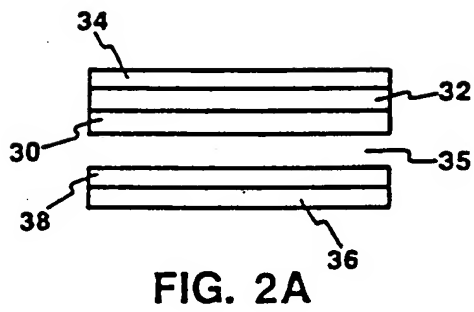
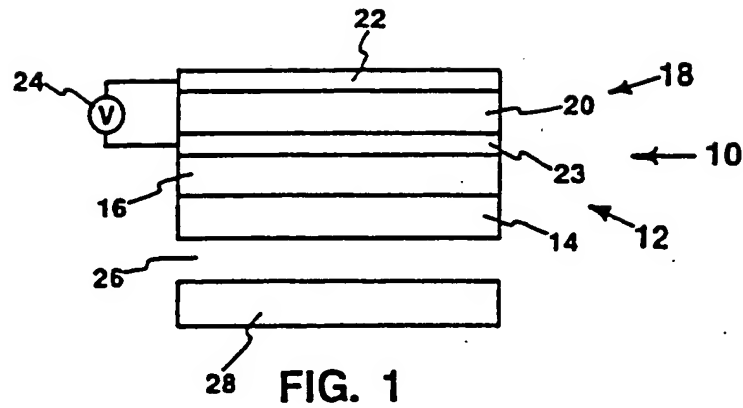
9. The sensor of Claim 8 wherein the detector is separated from the sensing chemistry by a sample flow channel.
10. The sensor of Claim 9 wherein the electroluminescent light source comprises a layer of electroluminescent material and means for applying a voltage to the layer.
11. The sensor of Claim 1 wherein the detector comprises a layer of conducting polymer and means for detecting a current produced therefrom by incident light.
12. The sensor of Claim 11 wherein the detector is a Shottky type detector, further comprising a pair of electrodes surrounding the conducting polymer.
13. The sensor of Claim 11 wherein the conducting polymer is p-type and the detector is a heterojunction/hybrid detector further comprising an n-type semiconductor layer adjacent to the polymer layer to form a p-n junction and a pair of electrodes surrounding the two adjacent layers.
14. A polymeric light detector, comprising:
 - a conducting polymer layer;
 - a pair of electrodes surrounding the polymer layer, at least one of which electrodes is transparent;
 - means connected to the electrodes for applying a voltage and for detecting an electric current produced in the polymer layer by incident light.
15. The detector of Claim 14 wherein the conducting polymer layer is photoconducting.
16. The detector of Claim 14 wherein the conducting polymer layer further comprises a photoconducting sublayer.

17. The detector of Claim 14 wherein the conducting polymer layer is p-type, and further comprising an n-type semiconductor layer adjacent to the polymer layer to form a p-n junction, wherein at least one of the polymer layer and semiconductor layer is photoconductive.
18. The detector of Claim 14 wherein the conducting polymer layer is about 1-100 μm thick.
19. The detector of Claim 16 wherein the sublayer thickness is about 5-10% of the thickness of the polymer layer.
20. The detector of Claim 14 wherein the polymer is selected from the group consisting of
- Polythiophene and its derivatives
 - Polyisothionaphthene
 - Trans-polyacetylene
 - Polyphenylene
 - Copolymer of pyrrole and quinone
 - Polyquinoline(s)
 - Polyaniline
 - Sulfonated polyaniline
 - Polyarylene vinylene
 - Polyvinylene
 - Polypyrrole and its derivatives
 - Poly(n-vinyl carbazole)
 - Polyphenylmethylsilylene-2,4,7-trinitro-9-fluorenone
 - Polytetrafluoroethylene
 - Copolymers of vinylidene fluoride and trifluoroethylene
 - Blends of polyvinylidene fluoride and polyalkylmethacrylate(s)
 - Poly(arylene azomethine)
 - Poly(arylene sulfurdiimide)
 - Poly(2-N-carbazolyethyl methacrylate)
 - Poly[S-(w-N carbazolyalkyl)L-Cysteine]

Poly(N-carbazolyethyl glycidyl ether)
Poly(N-methyl-3-hydroxymethylcarbazolyl
acrylate-co-
acryloyl-3'-hydroxypropyl 3,5
dinitrobenzoate)
Poly[N-(2-hydroxyethyl) carbazolyl
methacrylate-co-methacryloyl- β -hydroxyethyl
3,5-dinitrobenzoate]
Polymers incorporating metal phthalocyanin
moiety.

21. The detector of Claim 17 wherein the polymer layer is about 0.1-1.0 μm thick and the semiconductor layer is about 10-200 μm thick.
22. The detector of Claim 17 wherein the polymer layer is about 1-50 μm thick and the semiconductor layer is about 0.1-10 μm thick.
23. The detector of Claim 14 wherein the conducting polymer layer contains a dopant.
24. The detector of Claim 14 wherein the polymer is an inorganic polymer with a $\{P=N\}$ repeating unit.
25. An optical sensor comprising an optical transducer, a light source for inputting light into the transducer, and a detector for detecting light from the transducer, wherein at least one of (a) the light source is an electroluminescent light source comprising a layer of electroluminescent polymer and means for applying a voltage to the layer to produce light therefrom, and (b) the detector is a layer of photoconducting polymer and means for detecting a current produced therefrom by incident light.
26. The sensor of Claim 25 wherein either polymer is selected from the group consisting of

Polythiophene and its derivatives
Polyisothionaphthene
Trans-polyacetylene
Polyphenylene
Copolymer of pyrrole and quinone
Polyquinoline(s)
Polyaniline
Sulfonated polyaniline
Polyarylene vinylene
Polyvinylene
Polypyrrole and its derivatives
Poly(n-vinyl carbazole)
Polyphenylmethylsilylene/2,4,7-trinitro-9-fluorenone
Polytetrafluoroethylene
Copolymers of vinylidene fluoride and trifluoroethylene
Blends of polyvinylidene fluoride and polyalkylmethacrylate(s)
Poly(arylene azomethine)
Poly(arylene sulfurdiimide)
Poly(2-N-carbazolyethyl methacrylate)
Poly[S-(w-N carbazolyalkyl)L-Cysteine]
Poly(N-carbazolyethyl glycidyl ether)
Poly(N-methyl-3-hydroxymethylcarbazolyl acrylate-co-acryloyl-3'-hydroxypropyl 3,5-dinitrobenzoate)
Poly[N-(2-hydroxyethyl) carbazolyl methacrylate-co-methacryloyl- β -hydroxyethyl 3,5-dinitrobenzoate]
Polymers incorporating metal phthalocyanin moiety.



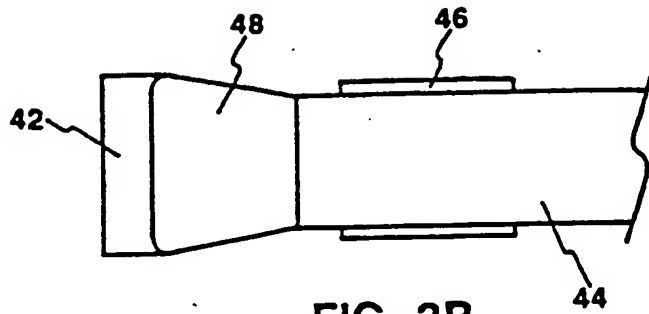


FIG. 3B

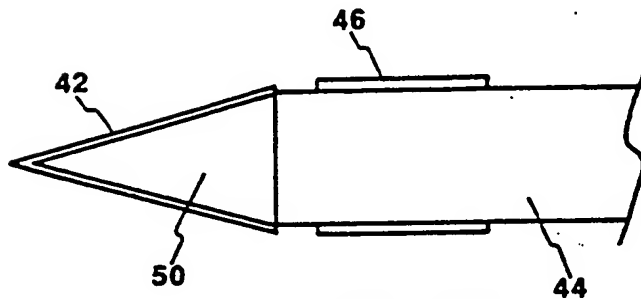


FIG. 3C

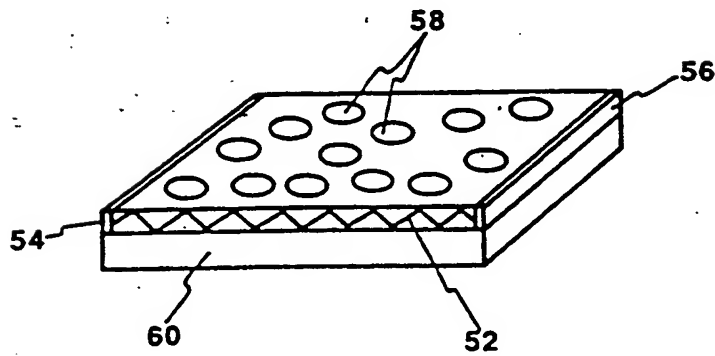


FIG. 4

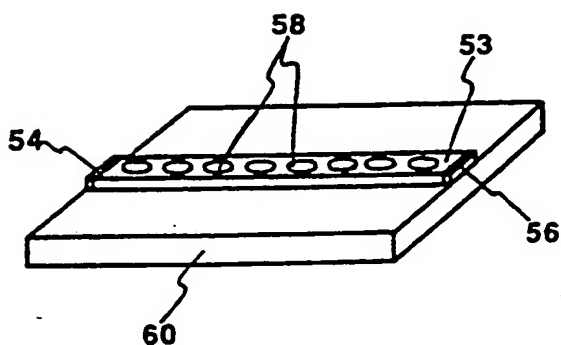


FIG. 5A

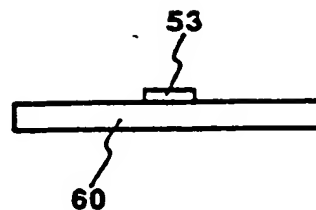


FIG. 5B

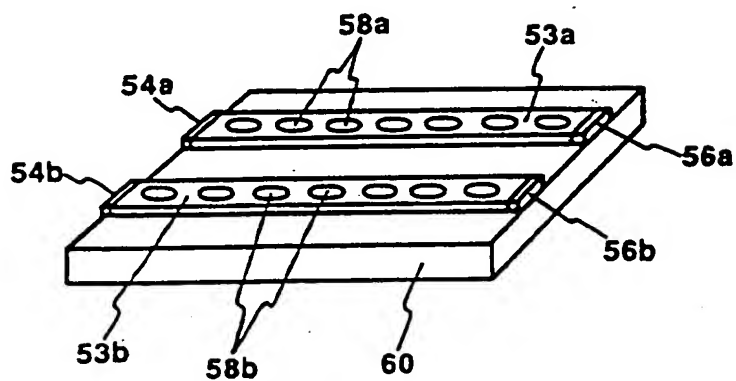


FIG. 5C

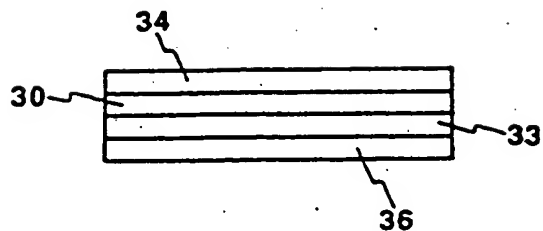


FIG. 6

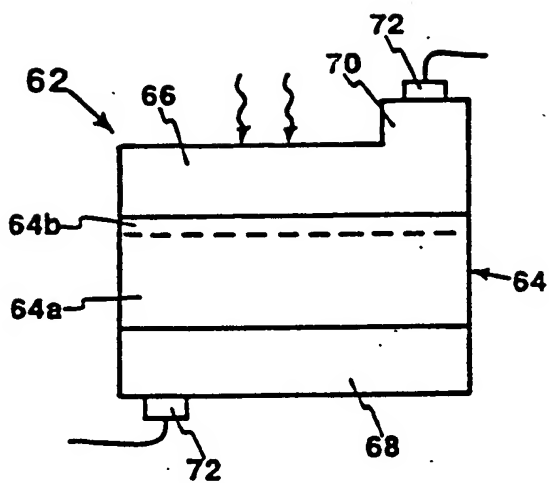


FIG. 7A

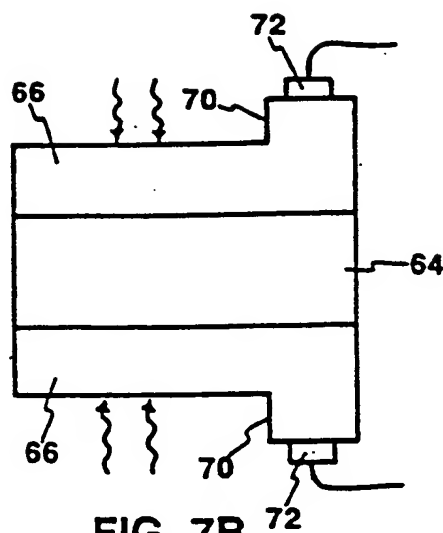


FIG. 7B

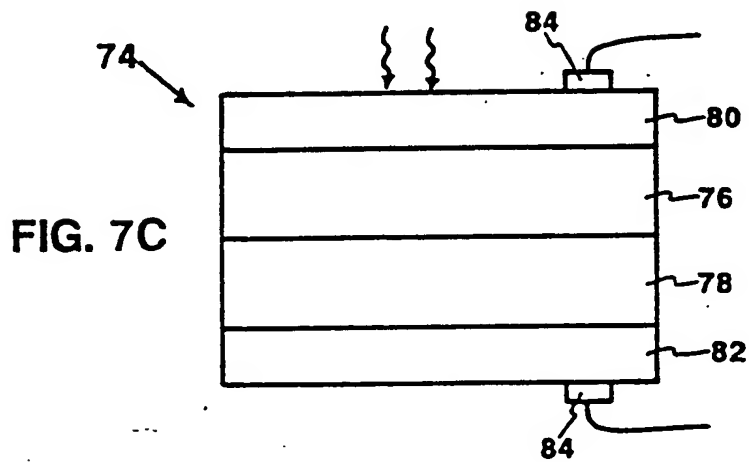


FIG. 7C

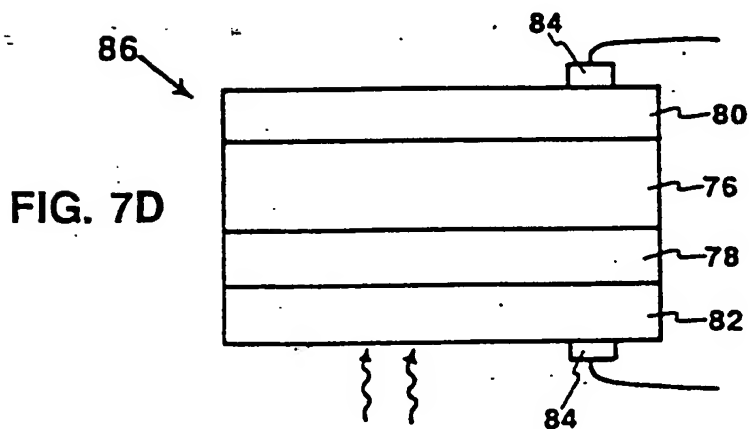


FIG. 7D

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/00368

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : H01L 27/14

US CL : 257/80

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 257/40, 80-85, 95, 98, 108, 453

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y | US, A, 5,158,619 (Kawada et al) 27 October 1992, especially column 2, lines 30-35. | 11-12, 14-24 |
| X/Y | US, A, 5,116,759 (Klainer et al) 26 May 1992, especially Figure 1. | 1-2, 5-10/ 1-26 |
| A | US, A, 5,107,104 (Miyasaka) 21 April 1992, entire document. | 1-26 |
| A | US, A, 5,059,790 (Klainer et al) 22 October 1991, entire document. | 1-26 |
| A | US, A, 4,829,345 (Ishioka et al) 09 May 1989, entire document. | 1-26 |
| A | US, A, 4,766,471 (Ovshinsky et al) 23 August 1988, entire document. | 1-26 |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | | |
|---|---|--|
| * Special categories of cited documents: | T | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
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| "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | A | document member of the same patent family |
| "O" document referring to an oral disclosure, use, exhibition or other means | | |
| "P" document published prior to the international filing date but later than the priority date claimed | | |

Date of the actual completion of the international search

06 APRIL 1994

Date of mailing of the international search report

19 APR 1994

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Telephone No. (703) 303-4916

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| Y | JP, B, 61-20372 (Mitsubishi Denki K.K.) 29 January 1986, see Abstract. | 13-24 |
| A | JP, B, 60-153183 (Matsushita Denki Sangyo K.K.) 12 August 1985, see Abstract. | 1-26 |
| A | JP, B, 59-2207041 (Toppan Printing K.K.) 12 December 1984, see Abstract. | 1-26 |
| A | Applied Physics Letters, Volume 60, No. 22, issued 01 June 1992, Y. Cao et al, "Solution-cast Films of Polyanilene: Optical-quality Transparent Electrodes", pages 11-13. | 1-26 |
| Y | Nature, Volume 357, issued 11 June 1992, G. Gustafsson et al, "Flexible Light-emitting Diodes Made from Soluble Conducting Polymers", pages 477-479. | 3,4,25,26 |
| A | Semiconductor International, issued January 1993, P. Singer, Ed., "Rapid Thermal Oxidation: Is It Viable?", page 2. | 1-26 |
| A | Advanced Materials, Volume 4, Number 1, issued January 1992, Grem et al, "Realization of a Blue-Light-Emitting Device Using Poly(p-phenylene)", pages 36-37. | 1-26 |